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(71) Applicant: CHEVRON U.S.A. INC. [US/US]; 3rd Floor, 2613 Camino Ramon, San Ramon, CA 94583-4289 (US).

(72) Inventors: O'REAR, Dennis, J.; 40 Upland Drive, Petaluma, CA 94952 (US). SCHINSKI, William, L.; 2818 Las Gallinas, San Rafael, CA 94903 (US).

(74) Agents: ZAVELL, A., Stephen et al.; Chevron Corporation, Law Dept., P.O. Box 6006, San Ramon, CA 94583-0806 (US).

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(54) Title: SYNTHESIS OF ALKYLBENZENES AND SYNLUBES FROM FISCHER-TROPSCH PRODUCTS
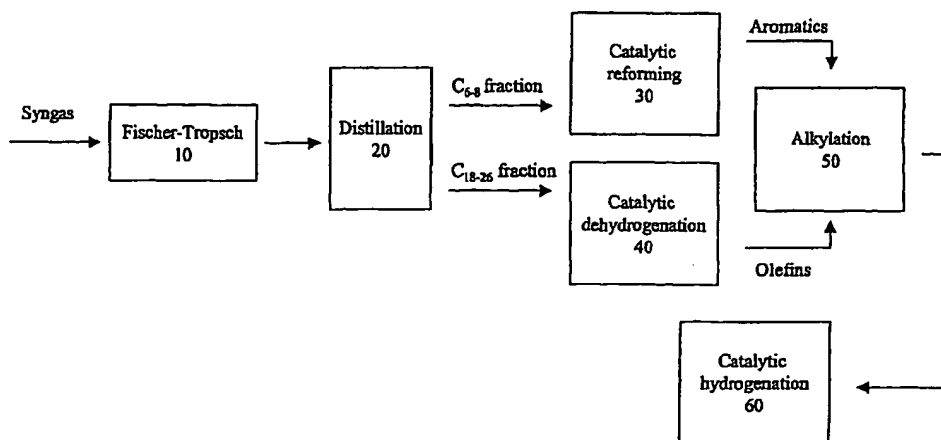
(57) Abstract: An integrated process for producing alkylbenzenes, sulfonated alkylbenzenes and/or alkylcyclohexanes from syngas is disclosed. The process involves subjecting syngas to Fischer-Tropsch conditions. Fractions rich in C_{6-8} and C_{18-26} hydrocarbons are isolated from the resulting product stream. The C_{6-8} fraction is subjected to catalytic reforming conditions to form aromatics. The C_{18-26} fraction may include sufficient olefins for use in an alkylation reaction with the aromatics. Optionally, the fraction may be subjected to dehydrogenation conditions to provide additional olefins. The resulting olefins are reacted with the aromatics in an alkylation reaction to yield alkylbenzenes. Unconverted olefins, paraffins, and aromatics can be obtained from the product stream via fractional distillation and recycled to form additional products. The alkylbenzenes can be hydrogenated to yield alkylcyclohexanes, which are useful as synlubes or as components in lube oil compositions. Alternatively, the alkylbenzenes can be sulfonated, and the resulting sulfonated alkylbenzenes used, for example, as detergents and/or dispersants.

1   **SYNTHESIS OF ALKYLBENZENES AND SYNLUBES**

2   **FROM FISCHER-TROPSCH PRODUCTS**

3

4   <u>BACKGROUND OF THE INVENTION</u>

5

6   There is a large demand for alkylbenzenes and synthetic lubricants

7   (synlubes). Alkylbenzenes are often used as detergents in a variety of

8   applications, for example, as lubricant oils. The preferred alkylbenzenes have

9   linear (as opposed to branched) alkyl groups, and are referred to as linear

10   alkylbenzenes. Linear alkylbenzenes are preferred over branched

11   alkylbenzenes because of their relatively high rate of biodegradability.

12

13   Currently, these products are prepared by alkylating normal alpha olefins

14   (NAOs), or isomerized olefins derived from normal alpha olefins, with benzene

15   or toluene. The NAOs are typically made from ethylene, which is a relatively

16   expensive raw material. Accordingly, the cost of the alkylbenzenes and

17   synlubes is relatively high. NAOs can also be prepared by wax cracking and

18   by modified ethylene oligomerization processes.

19

20   Linear alkylbenzenes can also be prepared from high purity unbranched

21   paraffins by dehydrogenating the paraffins to form olefins, and then alkylating

22   aromatic rings with the olefins. However, this approach is limited by the

23   relatively high cost of the paraffinic starting material and the limited supply of

24   high quality unbranched paraffins. If the paraffins are not extremely pure, but

25   rather, include isoparaffins or naphthenes, the catalysts tend to foul and the

26   products tend not to perform adequately.

27

28   One type of synthetic lubricant is derived from 1-decene that has been

29   trimerized and hydrogenated to form a T-shaped C_{30} isoparaffin. The

30   particular shape of the molecule provides it with a relatively high viscosity

31   index and low pour point, which is desirable for synthetic lubricants. However,

32   the decene trimer is not unique. Many alkylcyclohexanes also have relatively

-2-

1   high viscosity indexes (VI's) and low pour points (Briant et al., "Rheological

2   properties of lubricants", Editions Tecnip (Chapter 7 (1989).

3

4   It would be desirable to provide additional methods for forming alkylbenzenes

5   and alkylcyclohexanes. The present invention provides such methods.

6

7   SUMMARY OF THE INVENTION

8

9   In its broadest aspect, the present invention is directed to an integrated

10   process for preparing alkylbenzenes, sulfonated alkylbenzenes and/or

11   alkylcyclohexanes from syngas. In the first step, syngas is reacted under

12   Fischer-Tropsch conditions to form one or more product streams that include

13   C_{6-8} and C_{18-26} fractions. These fractions can be isolated, for example, via

14   conventional fractional distillation. Both fractions are optionally but preferably

15   treated, for example, by hydrotreating or extraction, to remove oxygenates

16   and other by-products of the Fischer-Tropsch synthesis.

17

18   The C_{6-8} fraction can be converted to aromatics via catalytic reforming

19   chemistry, preferably using the AROMAX® Process. The C_{6-8} fraction is ideal

20   for use in the AROMAX® Process, because it tends to have low levels of

21   sulfur, a known poison for the catalyst used in the AROMAX® Process.

22

23   The C_{18-26} fraction tends to be highly linear, and also has low levels of

24   impurities known to adversely affect processes for alkylating aromatics with

25   olefins. Depending on the particular Fischer-Tropsch conditions, the fraction

26   may include sufficient olefins and alcohols such that it can be directly reacted

27   with aromatics to form alkylbenzenes. The aromatics and C_{18-26} hydrocarbons

28   used to form the alkylbenzenes can be derived exclusively from the C_{6-8} and

29   C_{18-26} fractions from the Fischer-Tropsch reaction, or can optionally be

30   combined with aromatics and/or C_{18-26} hydrocarbons from other feedstocks,

1   assuming that the other feedstocks do not include impurities that would have

2   a detrimental effect on the subsequent chemistry.

3

4   The paraffinic portion of the $C_{18\text{-}26}$ fraction can be dehydrogenated to form

5   olefins and reacted with the aromatics. The alkylbenzenes can be used, for

6   example, as lubricant oils, or can be sulfonated to form detergents.

7

8   The alkylbenzenes can be reduced to form alkylcyclohexanes. In one

9   embodiment, the hydrogen produced during the catalytic reforming chemistry

10   can be used to hydrogenate the alkylbenzenes to form the alkylcyclohexanes.

11   The resulting alkylcyclohexanes can be used, for example, as synlubes or as

12   a component in synlube compositions. Preferably, the lubricant compositions,

13   including the alkylbenzenes and/or alkylcyclohexanes, also include

14   conventional lubricant additives.

15

16   In one embodiment, the Fischer-Tropsch chemistry is performed in two

17   separate reactors, in order to maximize the relative amounts of $C_{6\text{-}8}$ and $C_{18\text{-}26}$

18   fractions. The first reactor can be set up using conditions in which chain

19   growth probabilities are relatively low to moderate, and the product of the

20   reaction includes a relatively high proportion of low molecular ($C_{2\text{-}8}$) weight

21   olefins and a relatively low proportion of high molecular weight ($C_{30}+$) waxes.

22   This set of conditions optimizes yields of the $C_{6\text{-}8}$ fraction used to form the

23   aromatic rings which are to be alkylated with the $C_{18\text{-}26}$ paraffins. Preferred

24   catalysts are iron-containing catalysts.

25

26   The second reactor can be set up using conditions in which chain growth

27   probabilities are relatively high, and the product of the reaction includes a

28   relatively low proportion of low molecular ($C_{2\text{-}8}$) weight olefins and a relatively

29   high proportion of high molecular weight ($C_{30}+$) waxes. Preferred catalysts

30   are cobalt-containing catalysts. This set of conditions optimizes yields of the

31    $C_{18\text{-}26}$ fraction used to alkylate the aromatic rings.

32

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1	BRIEF DESCRIPTION OF THE DRAWINGS
2	
3	Figure 1 is a schematic flow diagram representing one embodiment of the
4	invention.
5	
6	DETAILED DESCRIPTION OF THE INVENTION
7	
8	The present invention is directed to an integrated process for producing
9	alkylbenzenes, sulfonated alkylbenzenes and/or alkylcyclohexanes from
10	syngas. As used herein, the term "integrated process" refers to a process
11	comprising a sequence of steps, some of which may be parallel to other steps
12	in the process, but which are interrelated or somehow dependent upon either
13	earlier or later steps in the total process.
14	
15	Fischer-Tropsch chemistry is used to convert the syngas to a product stream
16	which includes a C_{6-8} fraction and a C_{18-26} fraction. The Fischer-Tropsch
17	chemistry provides products which are highly linear and which include low
18	levels of sulfur. The C_{6-8} fraction is subjected to catalytic reforming conditions
19	for form C_{6-8} aromatics. The C_{18-26} fraction is dehydrogenated to form C_{18-26}
20	olefins, which are used to alkylate the C_{6-8} aromatics. The aromatics and
21	C_{18-26} hydrocarbons used to form the alkylbenzenes can be exclusively from
22	the Fischer-Tropsch reaction, or can optionally be combined with aromatics
23	and/or C_{18-26} hydrocarbons from other feedstocks. The resulting
24	alkylbenzenes can be used directly, or can be sulfonated to form sulfonated
25	alkylbenzenes or hydrogenated to form alkylcyclohexanes.
26	
27	Fischer-Tropsch Chemistry
28	
29	In Fischer-Tropsch chemistry, syngas is converted to liquid hydrocarbons by
30	contact with a Fischer-Tropsch catalyst under reactive conditions. Depending
31	on the quality of the syngas, it may be desirable to purify the syngas prior to
32	the Fischer-Tropsch reactor to remove carbon dioxide produced during the

1   syngas reaction and any sulfur compounds, if they have not already been

2   removed. This can be accomplished, for example, by contacting the syngas

3   with a mildly alkaline solution (e.g., aqueous potassium carbonate) in a

4   packed column.

5

6   Examples of conditions for performing Fischer-Tropsch type reactions are well

7   known to those of skill in the art. Suitable conditions are described, for

8   example, in U.S. Patent Nos. 4,704,487, 4,507,517, 4,599,474, 4,704,493,

9   4,709,108, 4,734,537, 4,814,533, 4,814,534 and 4,814,538, the contents of

10   each of which are hereby incorporated by reference in their entirety.

11

12   In general, Fischer-Tropsch catalysts contain a Group VIII transition metal on

13   a metal oxide support. The catalysts may also contain a noble metal

14   promoter(s) and/or crystalline molecular sieves. Certain catalysts are known

15   to provide chain growth probabilities that are relatively low to moderate, and

16   the reaction products include a relatively high proportion of low molecular

17   (C_{2-8}) weight olefins and a relatively low proportion of high molecular weight

18   ($C_{30}+$) waxes. Certain other catalysts are known to provide relatively high

19   chain growth probabilities, and the reaction products include a relatively low

20   proportion of low molecular (C_{2-8}) weight olefins and a relatively high

21   proportion of high molecular weight ($C_{30}+$) waxes. Such catalysts are well

22   known to those of skill in the art and can be readily obtained and/or prepared.

23   The product in the C_{18-26} range may include sufficient olefins and alcohols for

24   use in alkylation reactions with aromatics, depending on the Fischer-Tropsch

25   conditions. For example, Fischer-Tropsch reactions using an iron catalyst

26   and run at a relatively high temperature tend to provide a C_{18-26} fraction that

27   includes a sufficient amount of olefins for the alkylation reaction.

28

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1	<u>Catalyst Selection</u>
2	<u>Catalysts with low chain growth probabilities</u>
3	
4	In order to provide a product stream from a Fischer-Tropsch reaction including
5	a relatively large C_{6-8} fraction, any catalyst that provides relatively low to
6	moderate chain growth probabilities can be used. Typically, catalysts with an
7	alpha value between about 0.600 and 0.700 provide low chain growth
8	probabilities. Catalysts with an alpha value between about 0.700 and 0.800
9	provide moderate chain growth probabilities. Preferable catalysts are those
10	which tend to provide high yields (i.e., greater than about 20 and more
11	preferably greater than about 30 percent by weight of the products other than
12	methane) of light (C_{2-8}) alpha olefins.
13	
14	Preferred catalysts are iron-containing catalysts. Iron itself can be used and,
15	when iron oxides are formed, can be reduced with hydrogen back to iron.
16	However, because the presence of iron fines in the product stream is not
17	preferred, and because iron oxides (rust) decrease the surface area of the
18	catalyst available for reaction, other iron-containing catalysts may be
19	preferred. Examples of suitable iron-containing catalysts include those
20	described in U.S. Patent No. 4,544,674 to Fiato et al. and Xu et al., pp. 47-53,
21	*Chemtech* (Jan. 1998).
22	
23	In a preferred embodiment, the iron catalysts include at least about 10 to
24	about 60 weight percent iron. More preferably, they include between about 20
25	to about 60 weight percent iron, and most preferably about 30 to about
26	50 weight percent iron. These catalysts can be unsupported, but are
27	preferably promoted with a refractory metal oxide (SiO_2, Al_2O_3, etc.), alkali (K,
28	Na, Rb) and/or Group IB metals (Cu, Ag). These catalysts are usually
29	calcined, but usually are not reduced. Rather, they are brought up to reaction
30	temperature directly in the CO/H_2 feed.
31	

1 Co-precipitated iron-based catalysts, including those containing cobalt, can be
2 used. High levels of cobalt in an iron-cobalt alloy are known to produce
3 enhanced selectivity to olefinic products, as described, for example, in <u>Stud.</u>
4 <u>Surf. Sci. Catal.</u> 7, Pt/A, p. 432 (1981).
5
6 Examples of co-precipitated iron-cobalt catalysts and/or alloys include those
7 described in U.S. Patent Nos. 2,850,515, 2,686,195, 2,662,090, and
8 2,735,862; *AICHE* 1981 Summer Nat'l Meeting Preprint No. 408, "The
9 Synthesis of Light Hydrocarbons from CO and H_2 Mixtures over Selected
10 Metal Catalysts", ACS 173rd Symposium, Fuel Division, New Orleans, March
11 1977; *J. Catalysis* 1981, No. 72(1), pp. 37-50; Adv. Chem. Ser. 1981, 194,
12 573-88; Physics Reports (Section C of Physics Letters) 12 No. 5 (1974)
13 pp. 335-374; UK patent application No. 2050859A; *J. Catalysis* 72, 95-110
14 (1981); Gmelins Handbuch der Anorganische Chemie 8, Auflage (1959),
15 pg. 59; *Hydrocarbon Processing*, May 1983, pp. 88-96; and *Chem. Ing. Tech.*
16 49 (1977) No. 6, pp. 463-468.
17
18 Methods for producing high surface area metal oxides are described, for
19 example, in the French article, "<u>C. R. Acad. Sc. Paris</u>", p. 268 (28 May 1969)
20 by P. Courte and B. Delmon. Metal oxides with a high surface area are
21 prepared by evaporating to dryness aqueous solutions of the corresponding
22 glycolic acid, lactic acid, malic or tartaric acid metal salts. One oxide that was
23 prepared was $CoFe_2O_4$.
24
25 Iron-cobalt spinels which contain low levels of cobalt, in an iron/cobalt atomic
26 ratio of 7:1 to 35:1, are converted to Fischer-Tropsch catalysts upon reduction
27 and carbiding (see, for example, U.S. Patent No. 4,544,674 to Fiato et al.).
28 These catalysts tend to exhibit high activity and selectivity for C_2-C_6 olefins
29 and low methane production.
30
31 The contents of each of the patents and publications referred to above are
32 hereby incorporated by reference.

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1   <u>Catalysts with High Chain Growth Probabilities</u>

2

3   In order to provide a product stream from a Fischer-Tropsch reaction including

4   a relatively large C_{18-26} fraction, any catalyst that provides relatively high chain

5   growth probabilities can be used. Preferably, the catalyst used in the second

6   stage is a cobalt-containing catalyst. Ruthenium is also an effective

7   Fischer-Tropsch catalyst, but is more expensive.

8

9   One suitable cobalt catalyst that can be used is described in U.S. Patent

10   No. 4,579,986, as satisfying the relationship:

11

12                    $(3 + 4R) > L/S > (0.3 + 0.4R),$

13

14   wherein:

15

16   L = the total quantity of cobalt present on the catalyst, expressed as

17   mg Co/ml catalyst;

18   S = the surface area of the catalyst, expressed as m^2/ml catalyst; and

19   R = the weight ratio of the quantity of cobalt deposited on the catalyst

20   by kneading to the total quantity of cobalt present on the catalyst.

21

22   Other suitable catalysts include those described in U.S. Patent

23   Nos. 4,077,995, 4,039,302, 4,151,190, 4,088,671, 4,042,614 and 4,171,320.

24   U.S. Patent No. 4,077,995 discloses a catalyst that includes a sulfided mixture

25   of CoO, Al_2O_3 and ZnO. U.S. Patent No. 4,039,302 discloses a mixture of the

26   oxides of Co, Al, Zn and Mo. U.S. Patent No. 4,151,190 discloses a metal

27   oxide or sulfide of Mo, W, Re, Ru, Ni or Pt, plus an alkali or alkaline earth

28   metal, with Mo-K on carbon being preferred.

29

30   U.S. Patent No. 4,088,671 discloses minimizing methane production by using

31   a small amount of ruthenium on a cobalt catalyst. Supported ruthenium

1   catalysts suitable for hydrocarbon synthesis via Fischer-Tropsch reactions are

2   disclosed, for example, in U.S. Patent Nos. 4,042,614 and 4,171,320.

3

4   In general, the amount of cobalt present in the catalyst is between about 1

5   and about 50 weight percent of the total catalyst composition, more preferably

6   between about 10.0 and 25 weight percent.

7

8   Preferably, the catalyst contains between about 3 and 60 ppw cobalt, between

9   0.1 and 100 ppw of at least one of zirconium, titanium or chromium per

10   100 ppw of support (typically, silica, alumina, or silica-alumina and mixtures

11   thereof).

12

13   Catalyst Supports

14

15   The type of support used can influence methane production. Suitable metal

16   oxide supports or matrices which can be used to minimize methane

17   production include alumina, titania, silica, magnesium oxide, alkaline earth

18   titanates, alkali titanates, rare earth titanates and mixtures thereof.

19

20   Methane production can be decreased using supported ruthenium catalysts.

21   Titania or titania-containing supports provide lower methane production than,

22   for example, silica, alumina or manganese oxide supports. Accordingly,

23   titania and titania-containing supports are preferred.

24

25   Typically, the catalysts have a particle size of between 10 and 110 microns,

26   preferably between 20 and 80 microns, more preferably between 25 and

27   65 microns, and have a density of between 0.25 and 0.9 g/cc, preferably

28   between 0.3 and 0.75 g/cc. The catalysts typically include one or more of the

29   above-mentioned catalytic metals, preferably including iron in the first stage

30   and cobalt in the second stage, on one of the above-mentioned catalyst

31   supports. Preferably, the cobalt-containing catalysts include about 10 to

32   14 percent cobalt on a low density fluid support, for example, alumina, silica

1   and the like, having a density within the ranges set forth above for the

2   catalyst.

3

4   <u>Promoters and Noble Metals</u>

5

6   Methane selectivity is also influenced by the choice of promoter. Alkali metal

7   promoters are known for reducing the methane selectivities of iron catalysts.

8   Noble metals, such as ruthenium, supported on inorganic refractory oxide

9   supports, exhibit superior hydrocarbon synthesis characteristics with relatively

10   low methane production. Where a noble metal is used, platinum and

11   palladium are generally preferred. Accordingly, alkali metal promoters and/or

12   noble metals can be included in the catalyst bed of the first stage provided

13   that they do not significantly alter the reaction kinetics from slow chain growth

14   probabilities to fast chain growth probabilities.

15

16   The disclosures of each of the patents and articles discussed above are

17   incorporated herein by reference in their entirety.

18

19   <u>Operating Conditions</u>

20

21   Fischer-Tropsch reactions designed to produce a relatively high proportion of

22   the C_{6-8} fraction are typically conducted at temperatures between about 270°C

23   and 280°C, at a pressure of between about 1 and 20 ATM, in a slurry reactor

24   or a fluidized bed reactor. Typical synthesis gas linear velocity ranges in the

25   reactor are between about 2 and 40 cm per sec., preferably between about 6

26   and 10 cm per sec.

27

28   The products of the Fischer-Tropsch reaction include methane, C_{2-5}

29   hydrocarbons, C_6+ hydrocarbons, water and carbon dioxide, as well as

30   unreacted syngas. Water, methane, C_{2-5} hydrocarbons and carbon dioxide

31   are substantially removed to yield a product stream including mostly C_6+

1   hydrocarbons. The C_6+ hydrocarbons are predominantly C_{6-8} hydrocarbons,

2   which tend to be roughly 75% by weight olefins, and 25% by weight paraffins.

3   Optionally, but preferably, the product stream is hydrotreated at this stage to

4   remove any oxygenated products. If desired, the C_{6-8} hydrocarbons can be

5   isolated, for example, via distillation.

6

7   Fischer-Tropsch reactions designed to produce a relatively high proportion of

8   the C_{18-26} fraction are typically conducted in either a fixed bed reactor or a

9   slurry reactor, where slurry reactors are preferred. The operating temperature

10   of the fixed bed reactor is between about 200°C and 225°C, and the operating

11   temperature of the slurry reactor is between about 225°C and 250°C, with a

12   temperature around 240°C preferred. Typical synthesis gas linear velocity

13   ranges in the reactor are from about 2 to 40 cm per sec., preferably from

14   about 6 to 10 cm per sec. The pressure is preferably between about 1 and

15   30 ATM, with pressures between 20 and 30 ATM being particularly preferred.

16   Above about 30 ATM, carbonyls may be formed and, therefore, pressures

17   significantly above 30 ATM are not preferred. Further, the rate of reaction

18   tends to increase with increased pressure, but tends to level off due to

19   hydrodynamic problems at around 30 ATM.

20

21   The catalyst space velocities are typically between about 100 and

22   10,000 cc/g/h, preferably between about 300 and 3,000 cc/g/h, for both

23   stages.

24

25   The reaction mixture is preferably cooled to less than 100°C, and liquid

26   products are trapped. Methane is preferably bled off to a syngas generator

27   and recycled. Water is preferably removed.

28

29   The products of the Fischer-Tropsch reaction include methane, C_{2-50}

30   hydrocarbons, water and carbon dioxide, as well as unreacted syngas.

31   Water, methane, C_{2-17} hydrocarbons and carbon dioxide are substantially

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1   removed to yield a product stream including mostly $C_{18}+$ hydrocarbons. The

2    $C_{18}+$ hydrocarbons are mostly paraffinic. The desired C_{18-26} fraction can be

3   isolated, for example, by fractional distillation. Optionally, but preferably, the

4   fraction is hydrotreated at this stage to remove any oxygenated products.

5

6   Of course, the Fischer-Tropsch chemistry can be performed using only one

7   set of reaction conditions, and the C_{6-8} and C_{18-26} fractions can be isolated

8   from the product mixture as described above.

9

10   As discussed above, slurry reactors can be preferred for either set of

11   Fischer-Tropsch conditions. Bubble column slurry reactors can be particularly

12   preferred. Details regarding bubble column slurry reactors can be found, for

13   example, in Y. T. Shah et al., Design Parameters Estimations for Bubble

14   Column Reactors, *AIChE Journal*, 28 No. 3 pp. 353-379 (May 1982);

15   Ramachandran et al., Bubble Column Slurry Reactor, Three-Phase Catalytic

16   Reactors, Chapter 10, pp. 308-332 Gordon and Broch Science Publishers

17   (1983); Deckwer et al., Modeling the Fischer-Tropsch Synthesis in the Slurry

18   Phase, Ind. Eng. Chem. Process Des. Dev. v 21, No. 2, pp. 231-241 (1982);

19   Kölbel et al., The Fischer-Tropsch Synthesis in the Liquid Phase, Catal.

20   Rev.-Sci. Eng., v. 21(n), pp. 225-274 (1980); and U.S. Patent No. 5,348,982,

21   the contents of each of which are hereby incorporated by reference in their

22   entirety.

23

24   Since the catalyst metal may be present in the catalyst in the form of an oxide,

25   the catalyst may be reduced with hydrogen prior to contact with the slurry

26   liquid. The starting slurry liquid is typically a heavy hydrocarbon with a

27   viscosity sufficient to keep the catalyst particles suspended (typically between

28   4 and 100 centistokes at 100°C). The slurry liquid also has a low enough

29   volatility to avoid vaporization during operation (typically an initial boiling point

30   range of between about 350°C and 550°C). The slurry liquid is preferably

31   essentially free of contaminants such as sulfur, phosphorous or chlorine

-13-

1   compounds. Initially, it may be desirable to use a synthetic hydrocarbon fluid

2   such as a synthetic olefin oligomer as the slurry fluid.

3

4   Often, a paraffin fraction of the product having the desired viscosity and

5   volatility is recycled as the slurry liquid. The slurry typically has a catalyst

6   concentration of between about 2 and 40 percent catalyst, preferably between

7   about 5 and 20 percent, and more preferably between about 7 and 15 percent

8   catalyst based on the total weight of the catalyst, i.e., metal plus support.

9

10 Although the reactions described herein are described in terms of

11 Fischer-Tropsch reactions, they can optionally be performed using various

12 modifications of the literal Fischer-Tropsch process where hydrogen (or water)

13 and carbon monoxide (or carbon dioxide) are converted to hydrocarbons

14 (e.g., paraffins, ethers, etc.). Thus, the term Fischer-Tropsch type product or

15 process is intended to apply to Fischer-Tropsch processes and products and

16 the various modifications thereof and the products thereof. For example, the

17 term is intended to apply to the Kolbel-Engelhardt process typically described

18 by the reaction:

19

20                    $$3CO + H_2O \rightarrow -CH_2- + 2CO_2$$

21

22   The Separation of Product From the Fischer-Tropsch Reaction

23

24 The products from Fischer-Tropsch reactions generally include a gaseous

25 reaction product and a liquid reaction product. The gaseous reaction product

26 includes hydrocarbons boiling below about 650°F (e.g., tail gases through

27 middle distillates). The liquid reaction product (the condensate fraction)

28 includes hydrocarbons boiling above about 650°F (e.g., vacuum gas oil

29 through heavy paraffins).

30

1   The minus 650°F product can be separated into a tail gas fraction and a

2   condensate fraction, using, for example, a high pressure and/or lower

3   temperature vapor-liquid separator or low pressure separators or a

4   combination of separators. The condensate fraction includes about C_5 to C_{20}

5   normal paraffins and higher boiling hydrocarbons.

6

7   The fraction boiling above about 650°F (the condensate fraction) is typically

8   separated into a wax fraction boiling in the range of about 650°F-1200°F after

9   removing particulate catalyst fines and one or more fractions boiling above

10   about 1200°F. The wax fraction primarily contains C_{20} to C_{50} linear

11   hydrocarbons (paraffins, olefins and alcohols) with relatively small amounts of

12   higher boiling branched hydrocarbons. Typically, the separation is effected by

13   fractional distillation. The desired C_{6-8} and C_{18-26} fractions can be isolated

14   from the condensate and liquid fractions using techniques known to those of

15   skill in the art.

16

17   Optional Process Steps

18

19   The presence of sulfur, nitrogen, halogen, selenium, phosphorus and arsenic

20   contaminants in the feedstock is undesirable. For this reason, it is preferred

21   to remove sulfur and other contaminants from the feed before performing the

22   Fischer-Tropsch chemistry. Means for removing these contaminants are well

23   known to those of skill in the art. For example, ZnO guardbeds are preferred

24   for removing sulfur impurities. Means for removing other contaminants are

25   well known to those of skill in the art.

26

27   In one embodiment, any methane produced by the reaction is recovered and

28   converted to synthesis gas for recycling in the process. In some

29   embodiments, the product stream may contain a relatively large amount of

30   olefins that can be hydrogenated following the Fischer-Tropsch chemistry.

31

-15-

1   Removal of the methane and isolation of C_{6-8} and C_{18-26} fractions also

2   provides C_{9-17} and $C_{27}+$ fractions. The C_{9-17} fraction is in the diesel fuel range,

3   and can either be used directly, or alternatively, can be isomerized to improve

4   the pour point. Methods for isomerizing hydrocarbon feeds are well known to

5   those of skill in the art.

6

7   The $C_{27}+$ fraction can either be isolated and used directly, or can be reacted

8   to form lower molecular weight products, as desired. For example, the high

9   molecular weight products can be hydrocracked to provide lower molecular

10 weight products, which can be used, for example, as components in liquid

11 combustible fuels. The $C_{27}+$ fraction can also be converted into lube base

12 stocks by isomerization.

13

14 Hydrocracking refers to a catalytic process, usually carried out in the

15 presence of free hydrogen, in which the cracking of the larger hydrocarbon

16 molecules is a primary purpose of the operation. Desulfurization and/or

17 denitrification of the feed stock usually will also occur.

18

19 Catalysts used in carrying out hydrocracking operations are well known in the

20 art, and it should not be necessary to describe them in detail here. See, for

21 example, U.S. Patent Nos. 4,347,121 and 4,810,357 for general descriptions

22 of hydrotreating, hydrocracking, and typical catalysts used in each process.

23 The product from the hydrocracking can be subject to distillation and/or

24 catalytic isomerization to provide lube oils, diesel fuel, and the like.

25

26   Catalytic Reforming Processes Using the C_{6-8} Product Stream

27

28 The C_{6-8} product stream is reformed, for example, using catalytic reforming

29 conditions, to form aromatic products. Reforming is a complex process and

30 involves a number of competing processes or reaction sequences. These

31 include dehydrogenation of cyclohexanes to aromatics, dehydroisomerization

32 of alkylcyclopentanes to aromatics, dehydrocyclization of acyclic

1   hydrocarbons to aromatics, and hydrocracking of paraffins to light products

2   boiling outside the gasoline range. In addition, the dealkylation of

3   alkylbenzenes and the isomerization of paraffins occur in reforming

4   processes. As the C_{6-8} product stream includes predominantly acyclic

5   hydrocarbons, the major reforming reaction is dehydrocyclization.

6

7   Conditions suitable for reforming C_{6-8} product streams are well known in the

8   art, and include the AROMAX® Process and platforming or rheniforming

9   processes. The AROMAX® Process is well known to those of skill in the art,

10   and is described, for example, in *Petroleum & Petrochemical International*,

11   Volume 12, No. 12, pages 65 to 68, as well as U.S. Patent No. 4,456,527 to

12   Buss et al., the contents of which are hereby incorporated by reference.

13

14   These processes, their commercial startup conditions, and their useful range

15   of process operating conditions are all well known to those skilled in the art.

16   These processes can be carried out in a single reactor or in a series of

17   reactors.

18   '

19   Feedstock

20

21   The C_{6-8} fraction includes normal paraffins and alpha olefins and a minimum

22   of isoparaffins, and is used as at least a portion of the feedstock for the

23   catalytic reforming reaction. Isoparaffins can participate in the reaction if they

24   are not too highly branched, for example, like 2,2-dimethylbutane and

25   2,3-dimethylbutane. Accordingly, mono-alkylparaffins such as

26   mono-methylparaffins can be present in the feedstock. Several di- and

27   poly-alkylparaffins can also be present since they are relatively non-reactive

28   under the reaction conditions. Preferably, the stream includes predominantly

29   C_6 and C_7 hydrocarbons. Using the AROMAX® Process, yields of aromatic

30   compounds are nearly 90% when this stream is used.

31

-17-

1   As with the Fischer-Tropsch reaction described above, the feed should be

2   substantially free of sulfur, nitrogen, metals and other known poisons.

3   Methods for removing such poisons from the feed have been discussed

4   above. In a preferred embodiment, the C_{6-8} hydrocarbons contacting the

5   catalyst are substantially dry and free of sulfur, i.e., sulfur levels are preferably

6   maintained below about 50 ppb, preferably below about 25 ppb, and more

7   preferably below about 10 ppb. Sulfur removal systems are well known in the

8   ultra-low sulfur reforming art. If the product of the Fischer-Tropsch reaction in

9   the C_{6-8} range is combined with other feedstocks in that range, sulfur and

10   other impurities need to be removed.

11

12   Conversion Processes

13

14   The catalytic reforming process is a low sulfur reforming process, preferably

15   using a bound, halided Pt L-zeolite catalyst. Catalytic reforming is well

16   known. For example, it is described in the book, Catalytic Reforming, by

17   D. M. Little, PennWell Books (1985), which is incorporated herein by

18   reference in its entirety.

19   The reaction is preferably conducted at a temperature between 400°F and

20   1100°F, more preferably between 800°F and 1050°F. In the temperature

21   range of from 400°C to 600°C, the catalytic reforming reaction can occur with

22   acceptable speed and selectivity. When using traditional reforming catalysts,

23   if the operating temperature is below 400°C, the reaction speed is insufficient

24   and consequently the yield is too low for industrial purposes. When the

25   operating temperature is above 600°C, interfering secondary reactions such

26   as hydrocracking and coking may occur, reducing the yield. These secondary

27   reactions are minimized using the bound, halided, zeolite catalysts described

28   herein. They can also be minimized by incorporating an alkali metal, such as

29   potassium, or an alkaline earth metal, such as barium, strontium or calcium,

30   preferably barium, into the catalysts. The metals can be incorporated, for

1 example, via ion exchange, as described, for example, in U.S. Patent

2 No. 4,447,316 to Buss et al., the contents of which are hereby incorporated by

3 reference.

4

5 The pressure is preferably between 0 and 400 psig, more preferably between

6 15 and 150 psig. The recycle hydrogen rate is sufficient to yield a hydrogen

7 to hydrocarbon mole ratio for the feed to the reforming reaction zone between

8 0.1 and 20, more preferably between 0.5 and 10, and most preferably

9 between 2 and 6. The liquid hourly space velocity (LHSV) for the

10 hydrocarbon feed over the reforming catalyst is between 0.1 and 10 hr^{-1}, more

11 preferably between 0.5 and 5 hr^{-1}. Reforming produces hydrogen. Thus,

12 additional hydrogen is not needed except when the catalyst is reduced upon

13 startup, and when the feed is first introduced. Once reforming is underway,

14 part of the hydrogen that is produced is preferably recycled over the catalyst.

15

16 In one embodiment, aromatics are prepared by first preparing a halided

17 zeolite catalyst, bringing the catalyst on stream using commercial startup

18 conditions, and contacting the catalyst with the C_{6-8} paraffinic fraction at

19 catalytic reforming conditions to produce aromatics. The catalyst is preferably

20 prepared by washing a calcined, bound zeolite catalyst base with an aqueous

21 liquid, and adding at least one halogen-containing compound and a Group VIII

22 metal compound to the washed base.

23

24 In a preferred embodiment, the C_{6-8} fraction is converted to an aromatic

25 product stream by catalytic conversion of the C_{6-8} feed under conversion

26 conditions that include a commercial-type catalyst startup (at a low gas flow

27 rate and a slow heat-up rate). The process preferably uses a bound and

28 washed halided zeolite catalyst containing a Group VIII metal, where the

29 halided catalyst has a cycle length of >1200 hr following startup. The halided

30 catalyst is preferably prepared by a process that involves washing a bound

31 zeolite catalyst base or catalyst before halide addition and before reduction.

32

1   The feed can be contacted with the catalyst in a fixed bed system, a moving

2   bed system, a fluidized system, or a batch system. Either a fixed bed system

3   or a moving bed system is preferred. In a fixed bed system, the preheated

4   feed is passed into at least one reactor that contains a fixed bed of the

5   catalyst. The flow of the feed can be upward, downward or radial. The

6   effluent from the catalytic reforming reaction zone can be separated into the

7   desired streams or fractions.

8

9   Catalyst Selection

10

11   The catalysts used in the AROMAX® Process or similar catalytic reforming

12   processes are preferably bound and include a Group VIII metal, preferably Pt.

13   The catalysts are also preferably halided, and, more preferably, are (water)

14   washed, bound, halided catalysts. The term "catalyst" includes both the final

15   catalyst as well as precursors of the final catalyst. Precursors of the final

16   catalyst include, for example, the calcined form of the catalyst containing the

17   catalytic metal and also the catalyst prior to activation by reduction. As used

18   herein, the term "bound" is intended to describe a zeolite, binder combination

19   that is formed into aggregates such as pellets, pills, extrudates and the like.

20   The term "catalyst base", as used herein, refers to a bound zeolite.

21

22   Zeolites

23

24   Catalysts useful in the reforming reaction typically include one or more

25   zeolites or non-zeolitic molecular sieves and at least one catalytic metal,

26   preferably a Group VIII metal. The catalysts typically also include a binder

27   such as a refractory oxide, e.g., silica, alumina, chlorided alumina or silica-

28   alumina. Preferred zeolites and/or molecular sieves are selected from those

29   of the large and intermediate pore variety. The AROMAX® Process

30   traditionally uses PtBaK/L-zeolite as a catalyst. Traditional platforming and

31   rheniforming processes use Pt/Al_2O_3 or $PtRe/Al_2O_3$ as the catalyst. These

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1   and other catalysts and suitable reforming conditions are described, for

2   example, in U.S. Patent Nos. 3,546,102; 3,574,092; 3,679,575; 4,018,711;

3   4,104,320; 4,347,394; 4,370,224; 4,417,083; 4,434,311; 4,447,316 and

4   5,559,068.

5

6   Catalysts including platinum on chlorinated-alumina supports and Pt-X on

7   alumina or chlorinated-alumina supports, where X is rhenium, iridium or tin

8   have been used in catalytic reforming reactions. U.S. Pat. No. 4,370,224

9   discloses a multi-metallic reforming catalyst that includes platinum, iridium,

10   copper, selenium and halogen, composited with an inorganic oxide support or

11   carrier, preferably alumina. Zeolite-containing reforming catalysts, for

12   example, the zeolite mordenite, ZSM-type zeolites, zeolite L, Faujasites X and

13   Y, and the zeolite omega have been used.

14

15   Representative of the large pore zeolites are ZSM-3, ZSM-4, ZSM-10,

16   ZSM-12, ZSM-20, zeolite beta, zeolite omega, zeolite L, zeolite X, zeolite Y,

17   REY, USY, RE-USY, mordenite, LZ-210, LZ-210-M, LZ-210-T, LZ-210-A,

18   SSZ-24, SSZ-26, SSZ-31, SSZ-33, SSZ-35, SSZ-37, SSZ-41, SSZ-42,

19   SSZ-44 and MCM-58. ZSM-3 is described in U.S. Patent No. 3,415,736.

20   ZSM-4 is described in UK Application No. 1,117,568. ZSM-10 is described in

21   U.S. Patent No. 3,692,470. ZSM-12 is described in U.S. Patent

22   No. 3,832,449. ZSM-20 is described in U.S. Patent No. 3,972,983. Zeolite

23   beta is described in U.S. Patent No. Re. 28,341 (of original U.S. Patent

24   No. 3,308,069). Zeolite omega is described in U.S. Patent No. 4,241,036.

25   Zeolite L is described in U.S. Patent No. 3,216,789. Zeolite X is described in

26   U.S. Patent No. 2,882,244. Zeolite Y is described in U.S. Patent

27   No. 3,130,007. LZ-210, LZ-210-M, LZ-210-T, LZ-210-A and mixtures thereof

28   are described in U.S. Patent No. 4,534,853. SSZ-24 is described in U.S.

29   Patent No. 4,834,977. SSZ-26 is described in U.S. Patent No. 4,910,006.

30   SSZ-31 is described in U.S. Patent No. 5,106,801. SSZ-33 is described in

31   U.S. Patent No. 4,963,337. SSZ-35 is described in U.S. Patent

32   No. 5,316,753. SSZ-37 is described in U.S. Patent No. 5,254,514. SSZ-41 is

1   described in U.S. Patent No. 5,591,421. SSZ-42 is described in U.S. Serial

2   No. 08/199,040. SSZ-44 is described in U.S. Patent No. 5,580,540. MCM-58

3   is described in U.S. Patent No. 5,437,855. The entire contents of all these

4   patents and patent applications are incorporated herein by reference.

5

6   Preferably, the catalyst is an L-zeolite or a zeolite having an L-zeolite-type

7   channel structure and size, such as ECR-2 which is described in U.S. Patent

8   No. 4,552,731, and ECR-31 which is described in U.S. Patent No. 5,624,657

9   (Vaughan). Preferably, the catalyst is a monofunctional, non-acidic K

10   L-zeolite. Acidity in the L-zeolite generally leads to poor performance in

11   catalytic reforming. Examples of useful L-zeolites include those described in

12   U.S. Patent Nos. 3,216,789 (Breck), 4,552,731 (Vaughan), 4,544,539

13   (Wortel), 5,491,119 (Verduijn), and 4,530,824 (assigned to Tosoh Ltd.). The

14   entire contents of all these patents are incorporated herein by reference. One

15   useful non-acidic L-zeolite is manufactured by Union Oil Product (UOP),

16   Mobile, AL. A preferred non-acidic L-zeolite is manufactured by Tosoh Ltd.,

17   Japan, and sold under the name HSZ-500KOA. For these non-acidic zeolites,

18   potassium is a preferred cation; a preferred catalyst comprises K L-zeolite.

19   Preferred catalysts are monofunctional. They do not have the acid function of

20   conventional reforming catalysts. In contrast, conventional reforming

21   catalysts are bifunctional, with an acid and a metal function. Examples of

22   monofunctional catalysts include platinum on L-zeolite, wherein the L-zeolite

23   has been exchanged with an alkali metal, as disclosed in U.S. Patent

24   No. 4,104,320 to Bernard et al.; platinum on L-zeolite, wherein the L-zeolite

25   has been exchanged with an alkaline earth metal, as disclosed in U.S. Patent

26   No. 4,634,518 to Buss and Hughes; and platinum on L-zeolite as disclosed in

27   U.S. Patent No. 4,456,527 to Buss, Field and Robinson. The entire contents

28   of all these patents are incorporated herein by reference.

29

30   The term "non-acidic" is understood by those skilled in this area of art,

31   particularly by the contrast between monofunctional (non-acidic) reforming

1 catalysts and bifunctional (acidic) reforming catalysts. One method of

2 achieving non-acidity is by replacing protons with alkali and/or alkaline earth

3 metals in the zeolite. This is preferably achieved, along with other catalyst

4 enhancements, by an ion exchange process on the synthesized zeolite.

5

6 The composition of type L-zeolite expressed in terms of mole ratios of oxides,

7 may be represented by the following formula:

8

9 $$(0.9\text{-}1.3)M_{2/n}O\text{:}Al_2O_3(5.2\text{-}6.9)SiO_2\text{:}yH_2O$$
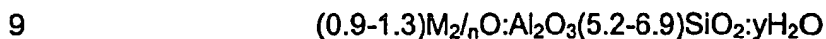
10

11 In the above formula, M represents a cation, n represents the valence of M,

12 and y may be any value from 0 to about 9. Zeolite L, its X-ray diffraction

13 pattern, its properties, and method for its preparation are described in detail

14 in, for example, U.S. Patent No. 3,216,789, the contents of which is hereby

15 incorporated by reference. The actual formula may vary without changing the

16 crystalline structure. For example, the mole ratio of silicon to aluminum (Si/Al)

17 may vary from 1.0 to 3.5.

18

19 As discussed above, one preferred embodiment of the invention uses

20 monofunctional Pt L-zeolite catalysts that have been treated with halogen-

21 containing compounds. This type of halogen treatment is known. For

22 example, U.S. Patent No. 5,091,351 to Murakawa et al. discloses preparing a

23 Pt L-zeolite catalyst, and then treating it with a halogen-containing compound.

24 Other related patents that disclose halided L-zeolite catalysts include

25 EP 498,182A or U.S. Patent No. 5,354,933, which discloses co-impregnation

26 of an L-zeolite with NH_4Cl and NH_4F; U.S. Patent Nos. 4,681,865, 4,761,512

27 and 5,073,652 to Katsuno et al. These patents are all incorporated herein by

28 reference. One preferred hiz-cat for catalytic reforming comprises halided

29 platinum K L-zeolite catalyst, especially one containing both chloride and

30 fluoride.

31

1   Examples of useful intermediate pore size zeolites include ZSM-5, ZSM-11,

2   ZSM-22, ZSM-23, ZSM-35, ZSM-48, ZSM-57, SUZ-4, SSZ-23; SSZ-25,

3   SSZ-28, SSZ-32 and SSZ-36. ZSM-5 is described in U.S. Patent

4   No. Re. 29,948 (of original U.S. Patent No. 3,702,886). ZSM-11 is described

5   in U.S. Patent No. 3,709,979. ZSM-22 is described in U.S. Patent

6   No. 4,556,477. ZSM-23 is described in U.S. Patent No. 4,076,842. ZSM-35

7   is described in U.S. Patent No. 4,016,245. ZSM-48 is described in U.S.

8   Patent No. 4,585,747. SUZ-4 is described in EP Application No. 353,915.

9   SSZ-23 is described in U.S. Patent No. 4,859,422. SSZ-25 is described in

10   U.S. Patent Nos. 4,827,667 and 5,202,014. SSZ-28 is described in U.S.

11   Patent No. 5,200,377. SSZ-32 is described in U.S. Patent No. 5,053,373.

12   SSZ-36 is described in U.S. Serial No. 60/034,252. The entire contents of all

13   these patents and patent applications are incorporated herein by reference.

14

15   In addition to silicon, the useful zeolites herein can contain one or more

16   framework elements other than, or in addition to, aluminum, e.g., the

17   borosilicate zeolites. Also, the zeolites can be modified to alter their

18   as-synthesized framework silica to alumina ratio.

19

20   Suitable catalysts can also include non-zeolitic molecular sieves with

21   intermediate or large size pores. Non-zeolitic molecular sieves are

22   microporous compositions that are formed from $[AlO_2]$ and $[PO_2]$ tetrahedra

23   and have electrovalently neutral frameworks. See U.S. Patent No. 4,861,743.

24   Also included among the useful zeolites are materials of similar structure or

25   behavior, e.g., crystalline metallophosphates such as those described in U.S.

26   Patent No. 4,440,871. Non-zeolitic molecular sieves include

27   aluminophosphates ($AlPO_4$) as described for example in U.S. Patent

28   No. 4,310,440, metalloaluminophosphates as described in U.S. Patent

29   Nos. 4,500,651; 4,567,029; 4,544,143; and 4,686,093, and non-metal

30   substituted aluminophosphates as described in U.S. Patent No. 4,973,785.

31

1   Useful catalysts also include intermediate pore silicoaluminophosphates

2   (SAPO's) as the non-zeolitic molecular sieve component. Intermediate pore

3   SAPO's include SAPO-11, SAPO-31, SAPO-41 and SM-3. U.S. Patent

4   No. 4,440,871 describes SAPO's generally and SAPO-11, SAPO-31 and

5   SAPO-41 specifically. The preparation of SM-3 and its unique characteristics

6   are described in U.S. Patent No. 5,158,665. All these patents are

7   incorporated herein by reference.

8

9   Binders

10

11   The zeolites and/or molecular sieves are bound. They are preferably

12   composited with matrix materials resistant to the temperatures and other

13   conditions employed in hydrocarbon conversion processes. Such matrix

14   materials can include active and inactive materials. Frequently, binders, such

15   as naturally occurring clays and inorganic oxides, are added to improve the

16   crush strength of the catalyst. The selection of binders and binding conditions

17   depends on the zeolite and its intended use.

18

19   Suitable binder materials include synthetic or naturally occurring zeolites,

20   alumina, clays such as montmorillonite and kaolin, and the refractory oxides

21   of metals of Groups IVA and IVB of the Periodic Table of the Elements.

22   Particularly useful are the oxides of silicon, titanium and zirconium, with silica

23   being preferred, especially low acidity silica. Combinations of such oxides

24   with other oxides are also useful, for example, silica-alumina, silica-magnesia,

25   silica-zirconia, silica-thoria, silica-beryllia, silica-titania, titania-zirconia, silica-

26   alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia and silica-

27   magnesia-zirconia. These oxides can be crystalline or amorphous, or can be

28   in the form of gelatinous precipitates, colloids, sols, or gels. Silica in the form

29   of a silica sol is a preferred binder. A preferred silica sol has about 30 wt. %

30   silica and contains small particles (7-9 nm in diameter), which result in

31   catalysts with good attrition resistance and excellent crush strengths.

32

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1   Extrusion aids and viscosity modifiers are generally used in addition to the

2   binders for forming pellets or extrudates from zeolites and/or molecular

3   sieves. These additives are typically organic compounds such as cellulose

4   based materials, for example, Methocel® sold by Dow Chemical Co., ethylene

5   glycol, and stearic acid. Many such compounds are known in the art. These

6   additives should not leave a detrimental residue, i.e., one with undesirable

7   reactivity or one that can block pores, after calcination. Preferably, the

8   residues do not add significant amounts of alkali or alkaline earth ash to the

9   catalyst. The above-described washing will remove low levels of these

10   materials. The residue from the extrusion aid is preferably less than a few

11   tenths of a percent by weight, more preferably less than 0.1 wt. %.

12

13   Methods for preparing catalyst compositions are well known to those skilled in

14   the art and include such conventional techniques as spray drying, pelletizing,

15   extrusion, various sphere-making techniques and the like. The methods of

16   in-extrudate formation of the zeolite/binder described in U.S. Patent

17   No. 5,558,851 to Miller and in U.S. Patent No. 5,514,362 can also be used.

18   The entire contents of these patents are incorporated herein by reference.

19

20   The relative proportions of zeolite to the binder/matrix can vary widely.

21   Generally, the zeolite content ranges from between about 1 to about 99 wt. %,

22   and more usually in the range of from about 5 to about 95 wt. %, of the dry

23   composite, more typically 50-85 wt. %.

24

25   Preferably, whole extrudates rather than crushed extrudates or unbound

26   zeolites are used. Bound zeolites reduce the pressure drop through a reactor,

27   provide improved flow rates, and are easier to load and unload. However, the

28   diffusion characteristics of whole extrudates are quite different from those of

29   unbound powdered zeolites. The interaction of a diffusing gas, such as a

30   halocarbon, is different for a powdered versus a bound zeolite. Diffusion

31   differences would also be especially significant if the catalyst evolves

32   materials such as gases or solids, for example during startup. Moreover, the

1   act of binding itself — including selecting binding materials and the binding

2   method — as well as calcining can affect catalyst performance. For example,

3   the binder can interact with the sieve by simply blocking internal and external

4   sites or by chemical interaction (e.g., alkali from a basic sieve like the

5   preferred L-zeolite of the present invention and silica are known to react under

6   thermal and hydrothermal calcination conditions). Moreover, the distribution

7   of impregnated materials may vary considerably on zeolite powder versus

8   bound zeolites. Thus, studies on powders alone cannot be used to predict

9   commercial performance of bound zeolite catalysts.

10

11   Group VIII Metal

12

13   The catalyst preferably includes at least one Group VIII metal, preferably a

14   noble metal (Pt, Pd, Rh, Ir, Ru, Os), and more preferably platinum. Group VIII

15   metal promoters; such as tin, germanium, cobalt, nickel, and combinations

16   thereof can also be used. Preferred amounts of metal are 0.1 to 5 wt. %,

17   more preferably 0.1 to 3 wt. %, and most preferably 0.3 to 1.5 wt. %, based on

18   the L-zeolite. Platinum compounds that form positively charged platinum

19   complex ions in solution are the preferred source of platinum. Platinum

20   tetraammine chloride and nitrate are especially preferred.

21

22   Additionally, one or more non-platinum group metals such as tin, indium and

23   Group VIIB metals such as rhenium can be added. Examples include Pt/Sn,

24   Pt/Pd, Pt/Ni, and Pt/Re. These metals can be readily introduced into the

25   composite employing a variety of known and conventional techniques, e.g.,

26   ion-exchange, incipient wetness, pore fill, impregnation, etc. Care should be

27   taken so that the Group VIII metal, e.g., platinum, is incorporated in a manner

28   that results in excellent and uniform dispersion. The incipient wetness

29   impregnation method is preferred.

30

1   Halides

2

3   The catalysts are preferably "hiz-cats," also referred to herein as "halided

4   catalysts" or "halided zeolite catalysts".   The term "hiz-cat" is intended to

5   include zeolite catalysts that result from adding halogen-containing

6   compounds to, or from halide impregnation of, zeolites, catalyst bases (i.e.,

7   bound zeolites) or zeolite catalysts (i.e., zeolites containing catalytic metal).

8   The halides of the hiz-cats are in addition to those that may be incorporated

9   into the catalyst from the catalytic metal source; that is, this halogen addition

10   or impregnation is not just that associated with conventional platinum loading

11   and impregnation, where platinum halides are often used. Nor does this

12   halogen treatment include conventional zeolite ion exchange operations.

13   Zeolite ion exchange sometimes uses a halide salt, such as KCl, to replace

14   the cations in the zeolite; this ion exchange can leave small amounts of halide

15   on the catalyst. Moreover, the term hiz-cat is not intended to include catalysts

16   where halide is added using alkali halides (e.g., KCl) or alkaline earth halides.

17   Added alkali is believed to be detrimental to hiz-cats performance.

18

19   The form in which the halide is present in hiz-cats is unknown, and may be as

20   ionic halide, neutral halide, or it may be part of a compound, such as a silica

21   halide or Pt halide. The term "halide" is used in a broad sense, and is not

22   intended to denote the ionic state of the added halogen or of the halogen

23   associated with the catalyst.

24

25   The halide can be chloride, fluoride, bromide, iodide, or combinations thereof.

26   Preferably, the hiz-cat contains chloride and/or fluoride, more preferably both.

27   Especially preferred hiz-cats can be prepared by treating the bound zeolite or

28   bound catalyst with halocarbons such as freons or with other chlorine-

29   containing and/or fluorine-containing compounds, e.g., by impregnation with

30   ammonium chloride and ammonium fluoride. Preferred hiz-cats useful in this

31   invention have high total halide after calcination (this includes all halides, e.g.,

32   both chloride and fluoride), i.e., they contain at least about 0.9 wt. % halide,

1   preferably at least about 1.1 wt. %, and more preferably at least about

2   1.3 wt. % total combined halide. More than about 5 wt. % halide does not

3   appear to provide significant advantages. When chloride and fluoride are

4   both present, the weight ratio of Cl to F can vary. Preferably, it is between

5   1:10 and 10:1. More preferably, chloride and fluoride are added in a weight

6   ratio of about 1:1.

7

8   The terms "chloride retensivity" and "retained chloride" denote the residual

9   chloride content of the catalyst after dry-out, reduction and about 300 hr

10   on-stream. Hiz-cats evolve chloride during these steps, especially during

11   reduction. Thereafter, the chloride level on the catalyst remains substantially

12   constant as the catalyst is brought on-stream and operated. After startup,

13   some halide does continue to evolve, but very slowly. Care should be taken

14   not to overheat the catalyst, (i.e., temperatures above about 950°F) since

15   additional chloride will evolve, and this overheating is not desirable.

16

17   Bound hiz-cat performance can be significantly improved by washing, for

18   example, with water, before the halide is added. Preferred catalysts retain

19   less of the added chloride than poor catalysts, even though the retained

20   chloride, i.e., the "chloride retensivity" is independent of startup conditions.

21   The sodium content of preferred catalysts is about 0.4 wt. %. Preferred

22   catalysts include less than about 0.5 wt. %, more preferably less than

23   0.45 wt. %, and most preferably less than 0.4 wt. % chloride.

24

25   Hiz-Cat Preparation

26

27   Hiz-cats can be prepared by extruding and then washing either the bound

28   catalyst or the catalyst base before halide addition. Preferably, the catalyst is

29   prepared by:

30

31   (a)   preparing a calcined silica-bound zeolite catalyst base;

1   (b)   washing the bound zeolite catalyst base with an aqueous liquid; and

2

3   (c)   incorporating a group VIII metal and halogen-containing compound(s)

4   comprising chlorine and fluorine into the washed base to produce a

5   halided zeolite catalyst.

6

7   Preferably, the catalyst is prepared using a low alkali, e.g., low sodium,

8   extrusion aid in step (a). The Pt and halogen-containing compounds can be

9   incorporated sequentially or, preferably, simultaneously. A calcined catalyst

10   base is preferably washed before adding the halogen-containing compounds

11   and the Group VIII metal, e.g., platinum. In this way, these added

12   components are not washed out of the catalyst. The catalyst base is

13   preferably washed with one or more volumes of wash water. The washing

14   desirably removes at least 20%, preferably at least 50%, of the readily

15   removable alkali.

16

17   Catalyst performance can also be improved by various ion exchange

18   processes. Cation exchange, such as with potassium and the like, often

19   includes a wash step. Hiz-cat performance is improved when the ion

20   exchange includes a wash step.

21

22   Isolation of Aromatic Products

23

24   Benzene, toluene and C_8 aromatic streams (i.e., xylenes and ethylbenzene)

25   can be recovered using conventional techniques such as distillation and

26   extraction.

27

28   Alkylation of the Aromatic Products

29

30   The alkylation of aromatics, as described herein, involves reaction of olefins

31   with aromatic rings in the presence of an acid catalyst. The reaction is similar

32   to Friedel-Crafts alkylation chemistry, except that an olefin, rather than a

1   haloalkane, is used to alkylate the aromatic rings. While C_{18-26} is the preferred

2   range of alkyl groups for the alkylation reaction, in some embodiments, it may

3   be desired to prepare other alkylbenzenes where the alkyl groups have

4   different molecular weight ranges, for example, C_{9-17} or C_{27-50}. The processes

5   described herein are also intended to include these embodiments.

6

7   The feedstock for the alkylation reaction as described herein is the C_{18-26}

8   fraction isolated from a Fischer-Tropsch reaction, which is mostly paraffinic. If

9   there are significant sulfur or solid impurities, these should be removed.

10   Moderate amounts of linear olefins (<40 mol. %) can be tolerated, as well as

11   linear alcohols (<40 mol. %). Both of these are capable of alkylating an

12   aromatic ring.

13

14   The paraffinic C_{18-26} fraction must be converted into olefins, for example, via

15   dehydrogenation chemistry.

16

17   Catalysts and conditions for the dehydrogenation of alkanes to form olefins

18   are well known to those of skill in the art and are described, for example, in

19   U.S. Patent No. 3,445,541 to Heckelsberg et al., U.S. Patent No. 3,856,876 to

20   Burnett, U.S. Patent No. 4,148,833 to Antos, U.S. Patent No. 4,420,649 to

21   Antos, U.S. Patent No. 4,476,344 to Kimble, U.S. Patent No. 4,827,066 to

22   Herber et al., U.S. Patent No. 4,482,646 to Eastman, U.S. Patent

23   No. 4,686,316 to Morrison, U.S. Patent No. 4,7516,342 to Kimble, U.S. Patent

24   No. 4,777,319 to Kung, U.S. Patent No. 4,778,942 to Vora et al., U.S. Patent

25   No. 4,798,911 to Lentz et al., U.S. Patent No. 4,827,066 to Herber et al., U.S.

26   Patent No. 4,827,072 to Imai et al., U.S. Patent No. 4,880,764 to Imai et al.,

27   U.S. Patent No. 4,897,253 to Jenkins, U.S. Patent No. 4,929,792 to Dessau,

28   U.S. Patent No. 4,956,517 to Johnson et al., U.S. Patent No. 4,973,779 to

29   Imai et al., U.S. Patent No. 4,982,047 to Barri et al., U.S. Patent

30   No. 5,012,027 to Abrevaya et al., U.S. Patent No. 5,143,886 to Iezzi et al.,

31   U.S. Patent No. 5,308,822 to Iezzi et al., U.S. Patent No. 5,321,192 to Cottrell

32   et al., U.S. Patent No. 5,430,220 to Khare et al., U.S. Patent No. 5,563,314 to

1   Agaskar et al., U.S. Patent No. 5,633,421 to Iezzi et al., U.S. Patent

2   No. 5,905,180 to Yokoyama et al., U.S. Patent No. 5,972,203 to Smith et al.,

3   European Patent Application 0 558 148 A1, and European Patent Application

4   0 560 437 A1, the contents of each of which are hereby incorporated by

5   reference.

6

7   Suitable dehydrogenation catalysts typically include a Group VIII metal from

8   the Periodic Table of the Elements, which includes iron, cobalt, nickel,

9   palladium, platinum, rhodium, ruthenium, osmium and iridium.

10

11   Platinum and palladium or the compounds thereof are preferred for use as

12   dehydrogenation catalysts, with platinum and compounds thereof being

13   especially preferred. When referring to a particular metal in this disclosure as

14   being useful, the metal may be present as an elemental metal or as a

15   compound of the metal. Reference to a particular metal is not intended to

16   limit the invention to any particular form of the metal unless the specific name

17   of the compound is given, as in the examples in which specific compounds

18   are named as being used in the preparations.

19

20   The process conditions selected for carrying out the dehydrogenation step will

21   depend upon the dehydrogenation catalyst used. In general, the pressure is

22   usually the lowest pressure consistent with the maintenance of catalyst

23   stability. The pressure is typically in the range of between about 0.1 and

24   10 atm, preferably between about 0.5 and 3 atm. The temperature is typically

25   between about 700°C to about 1200°F, with temperatures in the range of

26   between 800°F and 950°F being particularly preferred. The LHSV is typically

27   between 1 and 40 hr^{-1}, preferably between about 25 and 35 hr^{-1}. In the event

28   the catalyst deactivates with the time-on-stream, specific processes that are

29   well known to those skilled in art are available for the regeneration of the

30   catalysts. Any number of reactors for the dehydrogenation and alkylation

1   steps can be used, such as fixed bed, fluidized bed, ebulated bed, and the

2   like.

3

4   The dehydrogenation and alkylation reactions can occur in the same reactor,

5   since the presence of aromatics is not detrimental to the dehydrogenation

6   reaction. In this embodiment, the aromatic fraction and the C_{18-26} fraction are

7   combined in a single reactor that includes a dehydrogenation catalyst and an

8   alkylation catalyst. However, the product of the reaction may include alkyl

9   chains with more than one aromatic ring, resulting from dehydrogenation and

10   alkylation of the alkyl chain on the alkylbenzenes. For this reason, it can be

11   preferred to perform the dehydrogenation and alkylation reactions in separate

12   reactors, and, optionally, to remove any di-olefins from the olefin stream used

13   in the alkylation step.

14

15   The UOP Pacol and Detal processes are well-known process for alkylating

16   aromatics using a dehydrogenation catalyst (Pacol) and an alkylation catalyst

17   (Detal). These processes are described, for example, in Vora et al.,

18   Chemistry and Industry, 187-191 (1990), the contents of which are hereby

19   incorporated by reference. In the Pacol process, the conversion of n-paraffins

20   to mono-olefins is near equilibrium. A relatively small amount of the

21   n-paraffins is converted to di-olefins and aromatics. In the alkylation step,

22   diolefins produce di-phenylalkanes or heavier polymers, which tends to lower

23   the overall product yield. However, the amount of diolefins can be minimized,

24   for example, using the UOP DeFine process. The DeFine process is a

25   selective hydrogenation process that converts di-olefins to mono-olefins.

26

27   In a preferred embodiment, alkyl groups are subjected to dehydrogenation

28   conditions to form a product stream containing a mixture of unconverted   .

29   n-paraffins, mono-olefins and di-olefins. The product stream is reacted with a

30   selective catalyst to hydrogenate the di-olefins to mono-olefins. The

31   unconverted n-paraffins and mono-olefins are sent to a separate reactor along

32   with the aromatics. The preferred ratio of aromatics to olefins is between

1   about 2 and 50, preferably between 5 and 20. An alkylation catalyst, typically

2   a strong acid catalyst such as HF, sulfuric acid, an acidic ionic liquid such as a

3   quaternary amine-chloroaluminate salt, or an acidic zeolite catalyst, is used to

4   alkylate the aromatics. An example of an alkylation reaction is the UOP Detal

5   process.

6

7   Typically, the reaction products include unconverted paraffins, unconverted

8   aromatics, alkylbenzenes, heavy alkylate (aromatics with more than one alkyl

9   group) and polymers (formed from the acid-catalyzed polymerization of

10   olefins). The aromatics and unconverted paraffins can be obtained via

11   fractional distillation and recycled. The product can be separated from the

12   heavy alkylate via fractional distillation.

13

14   Additional details on the UOP Pacol, De Fine and Detal processes are

15   described, for example, in Schultz et al., "LAB Production, Second World

16   Conference on Detergents", Montreux, Switzerland, Oct. 5-19, 1986;

17   "Handbook of Petroleum Refining Processes," ed. R. Myers, New York,

18   McGraw-Hill, 1986; Vora et al., "Production of biodegradable detergent

19   intermediates," Second World Surfactants Congress, Paris, France,

20   May 24-27 (1988); and Broughton, "Adsorptive separations - liquids" in

21   "Kirk-Othmer Encyclopedia of Chemical Technology," Vol. 1, 3rd ed., New

22   York, John Wiley & Sons, 1978, the contents of which are hereby

23   incorporated by reference. Additional examples of alkylation chemistry are

24   described, for example, in EPA 0 731 072 by Chevron Chemical SA.

25

26   The resulting alkylbenzenes can be used directly, for example, as synthetic

27   lubricants (synlubes) and/or detergents in a variety of applications, for

28   example, as lubricant oils. Alternatively, they can be sulfonated to form

29   surfactants, or hydrogenated to form alkylcyclohexanes, which are useful in

30   synthetic lube oil compositions.

31

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1   Hydrogenation of Alkylbenzenes to form Alkylcyclohexanes

2

3   Conditions for hydrogenating benzene rings to form cyclohexane rings are

4   well known to those of skill in the art. Care must be taken to avoid

5   hydrocracking conditions, which might strip the alkyl groups from the ring.

6

7   Suitable catalysts and conditions for hydrogenating aromatic rings without

8   removing the alkyl side chains are well known in the art. Typical catalysts are

9   palladium or platinum catalysts on alumina or silica/alumina supports,

10   although ruthenium and rhodium catalysts can also be used. The reactions

11   are typically performed at a temperature between about 200°F and 500°F,

12   preferably around 300°F, under a hydrogen atmosphere at a pressure of

13   between about 100 and 500 psig.

14

15   Sulfonation of Alkylbenzenes to form sulfonated alkylbenzenes

16

17   Conditions for sulfonating alkylbenzenes are well known to those of skill in the

18   art and are described, for example, in EPA 0 731 072 by Chevron Chemical

19   SA, the contents of which are hereby incorporated by reference. In

20   EPA 0 731 072, alkylbenzenes are sulfonated by first forming sulfuric

21   anhydride, and then reacting the alkylbenzene with the sulfuric anhydride.

22   Sulfuric anhydride is formed by oxidizing sulfur dioxide at 450°C in the

23   presence of a vanadium oxide catalyst. The sulfonation reaction takes place

24   in a tube maintained at 65°C by falling film, where the sulfuric anhydride is

25   diluted with nitrogen and the alkylbenzene/sulfur dioxide ratio is maintained at

26   about 1.05. Residual sulfuric acid is then eliminated by thermal treatment

27   after dilution with about 10% of 100N oil, bubbling through nitrogen at the rate

28   of about 10 l/h/kg of product and agitating at 85°C, until a lower residual

29   sulfuric acid content is obtained (typically less than about 0.5%). The

30   resulting sulfonated alkylbenzenes can be used, for example, as detergents

31   and/or dispersants.

1   <u>Lube Oil Compositions</u>

2

3   The alkylcyclohexanes formed from the hydrogenation of the alkylbenzenes

4   are useful as lube oils or as components in lube oil compositions. The lube oil

5   compositions preferably have a kinematic viscosity of at least 3 centistokes,

6   more preferably at least 4 centistokes, still more preferably at least

7   5 centistokes, and most preferably at least 6 centistokes, where the viscosity

8   is measured at 40°C. They also have a viscosity index (a measure of the

9   resistance of viscosity change to changes in temperature) of at least 100,

10   preferably 140 or more, more preferably over 150, and most preferably over

11   160.

12

13   Another important property for the lube oil compositions is that they have a

14   relatively high flash point for safety reasons. Preferably, the flash point is

15   above 90°C, more preferably above 110°C, still more preferably greater than

16   175°C, and most preferably between 175°C and 300°C. The following table

17   (Table 1) shows a correlation between viscosity and flash point of preferred

18   lubricants for use in automobiles.

19

20   <u>Table 1</u>

Viscosity at 40°C (cSt)	Flash Point (D93), °C	Flash Point (D92), °C
3.0	175	175
4.08	205	208
4.18	201	214
6.93	230	237
11.03	251	269

21
22   *D92 and D93 listed in the above table refer to ASTM tests for measuring
23   flash point:
24
25   Flash Point, COC, °C   D 92
26   Flash Point, PMCC, °C   D 93
27

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1   The lube oil can be used, for example, in automobiles. The presence of the

2   aromatic or cyclohexane rings on the long alkyl chains gives it relatively high

3   additive solubility (the ability to dissolve lube oil additives) and seal swell

4   performance, relative to lube oils that do not include the aromatic or

5   cyclohexane rings. Seal swell (the ability to adsorb in gaskets that line the

6   lubricating system, causing them to swell slightly and make a good seal) is

7   higher for the alkylbenzenes and alkylcyclohexanes described herein than for

8   paraffinic lube oils that do not include these rings.

9

10   The lube oil can also be used as a blending component with other oils. This

11   can be particularly important when a lube oil includes alkylbenzenes of

12   alkylcyclohexanes in combination with pure paraffinic oils, where the

13   combination provides increased additive solubility and seal swell

14   characteristics. For example, the lube oil can be used as a blending

15   component with polyalphaolefins, or with mineral oils to improve the viscosity

16   and viscosity index properties of those oils, or can be combined with

17   isomerized petroleum wax. The lube oils can also be used as workover fluids,

18   packer fluids, coring fluids, completion fluids, and in other oil field and well-

19   servicing applications. For example, they can be used as spotting fluids to

20   unstick a drill pipe that has become stuck, or they can be used to replace part

21   or all of the expensive polyalphaolefin lubricating additives in downhole

22   applications. Additionally, they can also be used in drilling fluid formulations

23   where shale-swelling inhibition is important, such as those described in U.S.

24   Pat. No. 4,941,981 to Perricone et al.

25

26   Optional Components

27

28   The lube oil compositions include the alkylcyclohexanes, optionally include

29   conventional lubricants, and preferably also include various additives, such as

30   lubricants, emulsifiers, wetting agents, densifiers, fluid-loss additives, viscosity

31   modifiers, corrosion inhibitors, oxidation inhibitors, friction modifiers,

32   demulsifiers, anti-wear agents, dispersants, anti-foaming agents, pour point

1   depressants, detergents, rust inhibitors and the like. Other hydrocarbons,

2   such as those described in U.S. Patent No. 5,096,883 and/or U.S. Patent

3   No. 5,189,012, may be blended with the lube oil provided that the final blend

4   has the necessary pour point, kinematic viscosity, flash point, and toxicity

5   properties. The total amount of additives is preferably between 1-30 percent.

6   All percentages listed herein are weight percentages unless otherwise stated.

7

8   Examples of suitable lubricants include polyol esters of C_{12}-C_{28} acids.

9

10   Examples of viscosity modifying agents include polymers such as ethylene

11   alpha-olefin copolymers which generally have weight average molecular

12   weights of from about 10,000 to 1,000,000 as determined by gel permeation

13   chromatography.

14

15   Examples of suitable corrosion inhibitors include phosphosulfurized

16   hydrocarbons and the products obtained by reacting a phosphosulfurized

17   hydrocarbon with an alkaline earth metal oxide or hydroxide.

18

19   Examples of oxidation inhibitors include antioxidants such as alkaline earth

20   metal salts of alkylphenol thioesters having preferably C_5-C_{12} alkyl side chain

21   such as calcium nonylphenol sulfide, barium t-octylphenol sulfide,

22   dioctylphenylamine, as well as sulfurized or phosphosulfurized hydrocarbons.

23   Additional examples include oil soluble antioxidant copper compounds such

24   as copper salts of C_{10} to C_{18} oil soluble fatty acids.

25

26   Examples of friction modifiers include fatty acid esters and amides, glycerol

27   esters of dimerized fatty acids and succinate esters or metal salts thereof.

28

29   Dispersants are well known in the lubricating oil field and include high

30   molecular weight alkyl succinimides being the reaction products of oil soluble

31   polyisobutylene succinic anhydride with ethylene amines such as

32   tetraethylene pentamine and borated salts thereof.

1   Pour point depressants such as C_8-C_{18} dialkyl fumarate vinyl acetate

2   copolymers, polymethacrylates and wax naphthalene are well known to those

3   of skill in the art.

4

5   Examples of anti-foaming agents include polysiloxanes such as silicone oil

6   and polydimethyl siloxane; acrylate polymers are also suitable.

7

8   Examples of anti-wear agents include zinc dialkyldithiophosphate, zinc diaryl

9   diphosphate, and sulfurized isobutylene.

10

11   Examples of detergents and metal rust inhibitors include the metal salts of

12   sulfonic acids, alkylphenols, sulfurized alkylphenols, alkyl salicylates,

13   naphthenates and other oil soluble mono and dicarboxylic acids such as

14   tetrapropyl succinic anhydride. Neutral or highly basic metal salts such as

15   highly basic alkaline earth metal sulfonates (especially calcium and

16   magnesium salts) are frequently used as such detergents. Also useful is

17   nonylphenol sulfide. Similar materials made by reacting an alkylphenol with

18   commercial sulfur dichlorides. Suitable alkylphenol sulfides can also be

19   prepared by reacting alkylphenols with elemental sulfur. Also suitable as

20   detergents are neutral and basic salts of phenols, generally known as

21   phenates, wherein the phenol is generally an alkyl substituted phenolic group,

22   where the substituent is an aliphatic hydrocarbon group having about 4 to

23   400 carbon atoms.

24

25   Antioxidants can be added to the lube oil to neutralize or minimize oil

26   degradation chemistry. Examples of antioxidants include those described in

27   U.S. Pat. No. 5,200,101, which discloses certain amine/hindered phenol, acid

28   anhydride and thiol ester-derived products.

29

30   The combination of a metallic dithiophosphate hydroperoxide decomposer

31   and aminic antioxidant is reported to have a synergistic effect on lubricant

32   antioxidant performance. See Maleville et al., *Lubrication Science*, V9, No. 1,

1   pp. 3-60 (1996). Sulfur-substituted derivatives of mercapto carboxylic esters

2   also are reported to possess antioxidant properties. See M. A. Mirozopeva

3   et al., *Naftekhimiya*, V28, No. 6, pp. 831-837 (1988).

4

5   Additional lube oils additives are described in U.S. Patent No. 5,898,023 to

6   Francisco et al., the contents of which are hereby incorporated by reference.

7

8   The process will be readily understood by referring to the flow diagram in

9   Figure 1. In Figure 1, a mixture of carbon monoxide and hydrogen (syngas) is

10   added to a Fischer-Tropsch reactor (Box 10). A C_{6-8} fraction and a C_{18-26}

11   fraction are separately isolated via distillation (Box 20). The C_{6-8} fraction is

12   subjected to catalytic reforming to form aromatics and hydrogen gas (Box 30)

13   and the C_{18-26} fraction is dehydrogenated to form linear alpha olefins (Box 40).

14   The linear alpha olefins are used to alkylate the aromatics (Box 50), and the

15   resulting alkylbenzene compounds are optionally hydrogenated to form

16   alkylcyclohexanes (Box 60). In the flow scheme contained in Figure 1, the

17   process of the present invention is practiced in continuous operation.

18   However, it is possible to practice the present invention in batch operation.

1   WHAT IS CLAIMED IS:

2

3   1.   An integrated process for preparing alkylbenzenes, the process

4   comprising;

5

6   (a)   subjecting syngas to Fischer-Tropsch reaction conditions to form a

7   hydrocarbon product stream comprising olefins and paraffins;

8

9   (b)   isolating fractions rich in C_{6-8} and C_{18-26} hydrocarbons from the

10   product stream;

11

12   (c)   subjecting the fraction rich in C_{6-8} hydrocarbons to catalytic

13   reforming conditions to form C_{6-8} aromatics;

14

15   (d)   optionally subjecting the fraction rich in C_{18-26} hydrocarbons to

16   dehydrogenation conditions; and

17

18   (e)   alkylating the C_{6-8} aromatics with olefins in the C_{18-26} fraction.

19

20   2.   The process of claim 1, wherein the Fischer-Tropsch reaction conditions

21   are such that the fraction rich in C_{6-8} hydrocarbons is obtained from a

22   reaction where the catalyst provides low to moderate chain growth

23   probabilities.

24

25   3.   The process of claim 2, wherein the catalyst comprises iron.

26

27   4.   The process of claim 1, wherein the Fischer-Tropsch reaction conditions

28   are such that the fraction rich in C_{18-26} hydrocarbons is obtained from a

29   reaction where the catalyst provides high chain growth probabilities.

30

31   5.   The process of claim 4, wherein the catalyst comprises cobalt.

32

1   6.   The process of claim 1, wherein the catalytic reforming step is performed

2   using the AROMAX® Process.

3

4   7.   The process of claim 1, wherein the catalytic reforming step is performed

5   using platforming or rheniforming processes.

6

7   8.   The process of claim 1, wherein the dehydrogenation catalyst includes at

8   least one metal or a corresponding metal compound selected from the

9   group consisting of iron, cobalt, nickel, ruthenium, rhodium, palladium,

10   osmium, iridium and platinum.

11

12   9.   The process of claim 1, wherein the dehydrogenation catalyst

13   component comprises a noble metal or a compound thereof.

14

15   10.   The process of claim 9, wherein the noble metal is platinum or palladium

16   or a mixture of platinum and palladium or the compounds thereof.

17

18   11.   The process of claim 9, wherein the dehydrogenation/hydrogenation

19   component also contains rhenium or a compound of rhenium.

20

21   12.   The process of claim 1, further comprising isolating unreacted C_{18-26}

22   paraffins from the alkylation step, subjecting them to dehydrogenation

23   conditions, and recycling them in the alkylation step.

24

25   13.   The process of claim 1, wherein the alkylation reaction is performed

26   using the Detal process.

27

28   14.   The process of claim 1, wherein the aromatics used in the alkylation step

29   further comprise aromatics not derived from the fraction rich in C_{6-8}

30   hydrocarbons from the product stream in the Fischer-Tropsch step.

31

1   15.   The process of claim 1, wherein the C_{18-26} olefins used in the alkylation

2   step further comprise C_{18-26} olefins which are not derived from the

3   fraction rich in C_{18-26} hydrocarbons from the product stream in the

4   Fischer-Tropsch step.

5

6   16.   An alkylbenzene composition obtained by the steps of:

7

8   (a)   subjecting syngas to Fischer-Tropsch reaction conditions to form a

9   hydrocarbon product stream comprising olefins and paraffins;

10   (b)   isolating fractions rich in C_{6-8} and C_{18-26} hydrocarbons from the

11   product stream;

12

13   (c)   subjecting the fraction rich in C_{6-8} hydrocarbons to catalytic

14   reforming conditions to form C_{6-8} aromatics;

15

16   (d)   optionally subjecting the fraction rich in C_{18-26} hydrocarbons to

17   dehydrogenation conditions; and

18

19   (e)   alkylating the C_{6-8} aromatics with olefins in the C_{18-26} fraction to

20   form alkylbenzenes.

21

22   17.   An integrated process for preparing alkylcyclohexanes, the process

23   comprising;

24

25   (a)   subjecting syngas to Fischer-Tropsch reaction conditions to form a

26   hydrocarbon product stream comprising olefins and paraffins;

27

28   (b)   isolating fractions rich in C_{6-8} and C_{18-26} hydrocarbons from the

29   product stream;

30

1		(c)	subjecting the fraction rich in C_{6-8} hydrocarbons to catalytic
2			reforming conditions to form C_{6-8} aromatics;
3			
4		(d)	optionally subjecting the fraction rich in C_{18-26} hydrocarbons to
5			dehydrogenation conditions;
6			
7		(e)	alkylating the C_{6-8} aromatics with olefins in the C_{18-26} fraction to
8			form alkylbenzenes; and
9			
10		(f)	hydrogenating the alkylbenzenes to form alkylcyclohexanes.
11			
12	18.	The process of claim 17, wherein the Fischer-Tropsch reaction
13		conditions are such that the fraction rich in C_{6-8} hydrocarbons is obtained
14		from a reaction where the catalyst provides low to moderate chain
15		growth probabilities.
16		
17	19.	The process of claim 18, wherein the catalyst comprises iron.
18		
19	20.	The process of claim 17, wherein the Fischer-Tropsch reaction
20		conditions are such that the fraction rich in C_{18-26} hydrocarbons is
21		obtained from a reaction where the catalyst provides high chain growth
22		probabilities.
23		
24	21.	The process of claim 20, wherein the catalyst comprises cobalt.
25		
26	22.	The process of claim 17, wherein the catalytic reforming step is
27		performed using the AROMAX® Process.
28		
29	23.	The process of claim 17, wherein the catalytic reforming step is
30		performed using platforming or rheniforming processes.
31		

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1 24. The process of claim 17, wherein the dehydrogenation catalyst includes
2   at least one metal or a corresponding metal compound selected from the
3   group consisting of iron, cobalt, nickel, ruthenium, rhodium, palladium,
4   osmium, iridium and platinum.

5

6 25. The process of claim 17, wherein the dehydrogenation catalyst
7   component comprises a noble metal or a compound thereof.

8

9 26. The process of claim 25, wherein the noble metal is platinum or
10   palladium or a mixture of platinum and palladium or the compounds
11   thereof.

12

13 27. The process of claim 24, wherein the dehydrogenation/hydrogenation
14   component also contains rhenium or a compound of rhenium.

15

16 28. The process of claim 17, further comprising isolating unreacted C_{18-26}
17   paraffins from the alkylation step, subjecting them to dehydrogenation
18   conditions, and recycling them in the alkylation step.

19

20 29. The process of claim 17, wherein the alkylation reaction is performed
21   using the Detal process.

22

23 30. An alkylcyclohexane composition obtained by the steps of:

24

25   (a) subjecting syngas to Fischer-Tropsch reaction conditions to form a
26   hydrocarbon product stream comprising olefins and paraffins;

27

28   (b) isolating fractions rich in C_{6-8} and C_{18-26} hydrocarbons from the
29   product stream;

30

31   (c) subjecting the fraction rich in C_{6-8} hydrocarbons to catalytic
32   reforming conditions to form C_{6-8} aromatics;

1   (d)   optionally subjecting the fraction rich in C$_{18-26}$ hydrocarbons to
2   dehydrogenation conditions;
3
4   (e)   alkylating the C$_{6-8}$ aromatics with the olefins in the C$_{18-26}$ fraction to
5   form alkylbenzenes; and
6
7   (f)   hydrogenating the alkylbenzenes to form alkylcyclohexanes.
8
9   31. The composition of claim 30, further comprising one or more lube oil
10   additives selected from the group consisting of lubricants, emulsifiers,
11   wetting agents, densifiers, fluid-loss additives, viscosity modifiers,
12   corrosion inhibitors, oxidation inhibitors, friction modifiers, demulsifiers,
13   anti-wear agents, dispersants, anti-foaming agents, pour point
14   depressants, detergents, and rust inhibitors.
15
16   32. A sulfonated alkylbenzene composition obtained by the steps of:
17
18   (a)   subjecting syngas to Fischer-Tropsch reaction conditions to form a
19   hydrocarbon product stream comprising olefins and paraffins;
20
21   (b)   isolating fractions rich in C$_{6-8}$ and C$_{18-26}$ hydrocarbons from the
22   product stream;
23
24   (c)   subjecting the fraction rich in C$_{6-8}$ hydrocarbons to catalytic
25   reforming conditions to form C$_{6-8}$ aromatics;
26
27   (d)   optionally subjecting the fraction rich in C$_{18-26}$ hydrocarbons to
28   dehydrogenation conditions;
29
30   (e)   alkylating the C$_{6-8}$ aromatics with the olefins in the C$_{18-26}$ fraction to
31   form alkylbenzenes; and
32

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1   (f)   sulfonating the alkylbenzenes to form sulfonated alkylbenzenes.

2

3   33.   A method for enhancing the additive solubility and/or seal swell

4   performance of a paraffinic lube oil composition comprising adding an

5   effective additive solubility enhancing and/or seal swell performance

6   enhancing amount of an alkylcyclohexane and/or alkylbenzene

7   composition to the paraffinic lube oil composition.

8

9   34.   The method of claim 33, wherein the alkylbenzene composition is

10   obtained by the steps of:

11

12   (a)   subjecting syngas to Fischer-Tropsch reaction conditions to form a

13   hydrocarbon product stream comprising olefins and paraffins;

14

15   (b)   isolating fractions rich in C_{6-8} and C_{18-26} hydrocarbons from the

16   product stream;

17

18   (c)   subjecting the fraction rich in C_{6-8} hydrocarbons to catalytic

19   reforming conditions to form C_{6-8} aromatics;

20

21   (d)   optionally subjecting the fraction rich in C_{18-26} hydrocarbons to

22   dehydrogenation conditions; and

23

24   (e)   alkylating the C_{6-8} aromatics with the olefins in the C_{18-26} fraction to

25   form alkylbenzenes.

26

27 35.   The method of claim 33, wherein the alkylcyclohexane composition is

28   obtained by the steps of:

29

30   (a)   subjecting syngas to Fischer-Tropsch reaction conditions to form a

31   hydrocarbon product stream comprising olefins and paraffins;

32

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1   (b)   isolating fractions rich in C_{6-8} and C_{18-26} hydrocarbons from the

2   product stream;

3

4   (c)   subjecting the fraction rich in C_{6-8} hydrocarbons to catalytic

5   reforming conditions to form C_{6-8} aromatics;

6

7   (d)   optionally subjecting the fraction rich in C_{18-26} hydrocarbons to

8   dehydrogenation conditions;

9

10   (e)   alkylating the C_{6-8} aromatics with the olefins in the C_{18-26} fraction to

11   form alkylbenzenes; and

12

13   (f)   hydrogenating the alkylbenzenes to form alkylcyclohexanes.
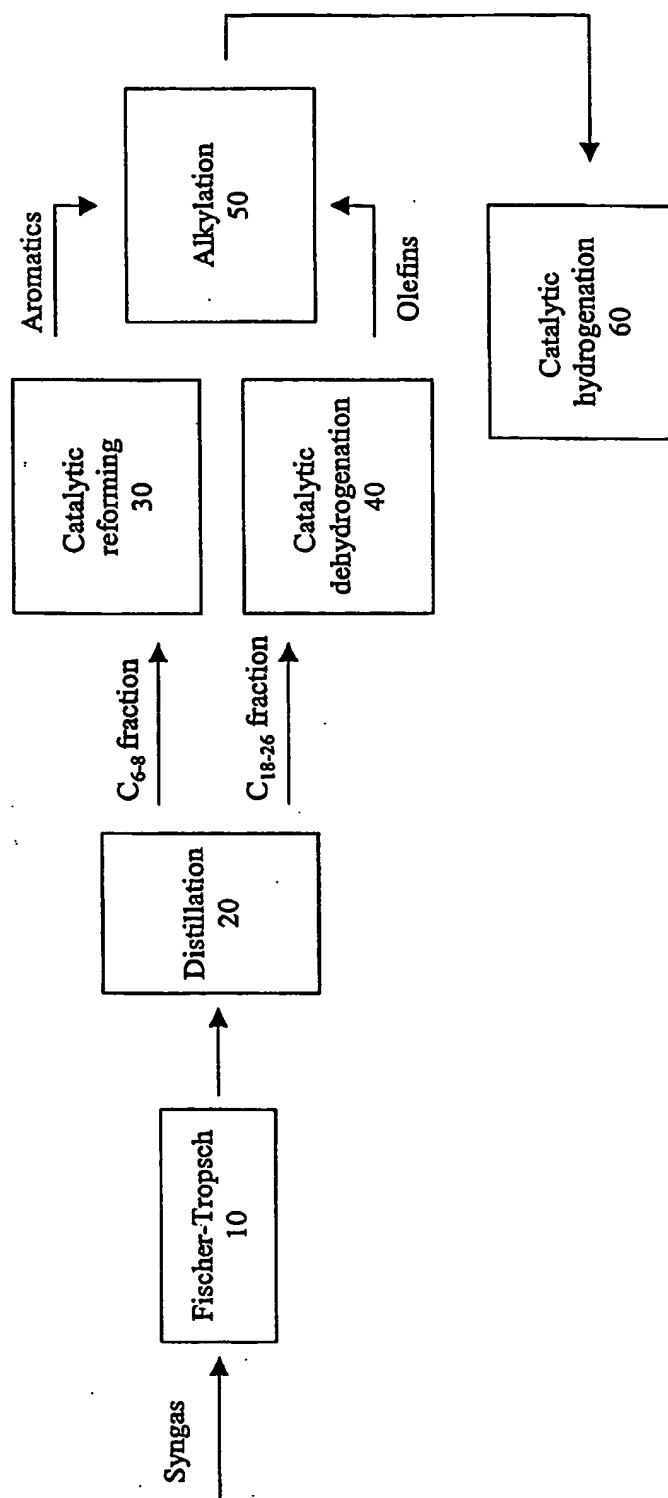
Figure 1

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7   C07C15/107   C07C13/18   C07C309/31   C10M127/02   C10M127/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7   C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A,P	WO 01 02325 A (SASOL TECHNOLOGY; DE WET EWALD WATERMEYER) 11 January 2001 (2001-01-11) claims	1,16
A	GB 669 313 A (CALIFORNIA RESEARCH CORP) 2 April 1952 (1952-04-02) claims	32

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search	Date of mailing of the international search report
6 June 2001	18/06/2001

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Van Geyt, J

1

INTERNATIONAL SEARCH REPORT

'ormation on patent family members

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
WO 0102325	A	11-01-2001	AU	6541100 A	22-01-2001
GB 669313	A	02-04-1952	NONE		